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REFINING OF *PINE RADIATA* AND EUCALYPTUS KRAFT PULPS ASSISTED WITH COMMERCIAL LACCASE MEDIATOR SYSTEMS

Authors*: Michael Lecourt[1]
Adrien Soranzo[1]
Michel Petit-Conil[2]

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SUMMARY

In the manufacture of papers, an important step is the refining of the pulp to develop the strength properties. Today, to decrease the operating costs, one way is to apply enzymes on the pulp before refining. The objective of our work was to introduce laccase treatment to reduce the electrical energy consumption and to enhance the pulp properties.

On a eucalyptus bleached kraft pulp, laccase associated to syringaldehyde or a new mediator affected the refining behaviour. Lower bulk values were measured for the biotreated pulps, fibres were more flexible and more amenable to compaction during the sheet formation. The tensile strength was improved with the new mediator and laccase treatments. Besides, some impact on the fibre intrinsic strength was observed. The laccase associated to the new mediator allowed to enhance both breaking length and tear index.

On a *Pine radiata* unbleached kraft pulp, the laccase, alone or associated to the new mediator, facilitated the refining. Breaking length was enhanced at a given energy consumption. The fibres were more amenable to the mechanical action and fibre fibrillation and cutting requested less energy. This was confirmed by the higher macrofibrillation index observed on the refined biotreated pulps.

INTRODUCTION

Paper production is a complex process aiming at producing paper sheets from fibres of various origins with maximum strength at the lowest cost. After pulping, fibres do not present enough bonding strength. Consequently, a mechanical treatment, i.e. refining, is required to increase fibre bonding and develop paper strengths (Scott, Abbott 1995). However, such a treatment is highly energy consuming. Today, because of cost reductions and environmental regulations, paper producers need to reduce energy consumption in refining. Different solutions were developed, such as adapting plate pattern to modify fibre treatment (Radoslavova, Roux 1997; Seth, 1999; Manfredi, 2004) or varying consistency (dos Reis, 2002). Other methods consisted in increasing flow through refiner or redesigning refining strategy (Gabl, Gorton 2004). Nevertheless, these methods require important investments. Thus, a simpler method had to be found. It should request limited changes in process, neither interact with wet end chemistry. Enzymes seemed to be a good alternative. Biotechnology was introduced in the early 1970s with objective to increase paper process profitability through more efficient steps in the process. Hence, focus was paid to reduce energy consumption during mechanical (Hoddenbagh, Meyer 2007; Maijala, 2008; Meyer, Petit-Conil 2009) or semi-mechanical pulping (Zhang, Chen 2009), chemical consumption during bleaching stage (Viikari, Ranua 1986) or to limit pitch problems (Irie, Matsukura 1989; Shouqin, Yiting 2001).

This work was inspired by results obtained treating bleached kraft pulps with cellulases (Lecourt, Sigoillot 2010; Lecourt, Sigoillot 2010). In the present work, the impact of a laccase pre-treatment before disc refining at pilot scale of unbleached kraft pulps was studied. Various mediators were applied on two kraft pulps, and refining parameters were studied on a pilot scale disc refiner allowing an accurate simulation of industrial refining.

MATERIALS AND METHODS

Pulp treated

Pulp was disintegrated and fibres dispersed in a slusher at a temperature of 40°C.

Market bleached eucalyptus kraft pulp, from Spain.

Market unbleached *Pine radiata* kraft pulp, from Chile.

Authors' references:

1. InTechFibres – FCBA, BP 254, 38044 Grenoble, France; Phone: 04 76 76 10 10, Fax : 04 76 76 10 15
2. InTechFibres – CTP, BP 254, 38044 Grenoble, France

Autor correspondente / Corresponding author: Michael Lecourt – E-mail: michael.lecourt@fcba.fr

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Pulp enzymatic pre-treatments

Laccase - supplied by Novozyme (NS51003) - was used in combination with various mediators: syringaldehyde (SA) or a new mediation (NM).

Laccase solution was added in the pulp suspension during the slushing step, before refining, at a pulp consistency of 4.5%. In order to match with industrial conditions, temperature was fixed at 40°C and treatment time at 30 min. pH was neutral without adjustment. Depending on conditions to be tested, a mediator was added to laccase in order to boost the efficiency. This mediator was introduced just after dispersing the enzyme solution in the pulp in slusher with a charge of 2%.

Results obtained by using mediator were compared to control, namely refining performed on fibre slushed only in water.

Pilot refining

Trials were performed on a 12" single-disc refiner pilot system. 5 kg of o.d. pulp were used to obtain each refining curve. The disc refiner was equipped with a plate pattern allowing reaching a specific edge load of 0.4 Ws/m for eucalyptus pulp and 1.9 Ws/m for *Pine radiata*. Edge load is defined as the ratio of motor power *versus* plate cutting length and represents the intensity of treatments applied on the fibres. One tank was used to store the pulp before refining. A pump conveyed the suspension into the refiner, in between the plates. A flow meter and a pressure controller are used to adjust refining conditions and to insure a good reproducibility. The refined pulp was collected in a second tank. Consequently, refinings were run in successive stages, the total amount of pulp being refined during each stage. Pulp was sampled after each run, allowing the determination of pulp characteristics corresponding to one point of refining curves (**Figure 1**).

Several runs were necessary to reach the desired final drainage index - Schopper-Riegler index (°SR) -, and to obtain the refining curve. Motor load was measured all along processing and specific energy consumption (SEC) calculated. Treatments were repeated twice in order to evaluate the reproducibility of results. Standard deviations were calculated for each refining points.

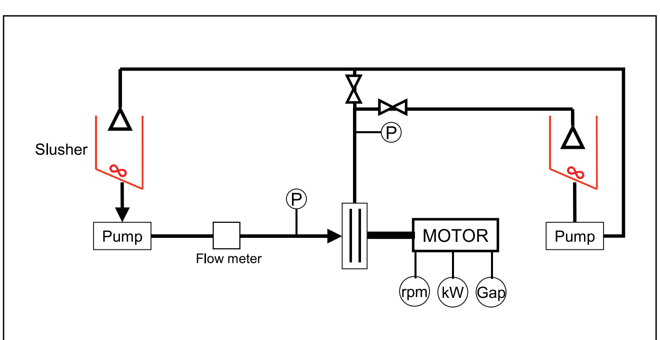

Figure 1. Flowsheet of the low consistency refiner installation

Pulp quality evaluation

Energy consumption, drainage index (NF ISO 5267-1) were measured, as they are used as refining control parameters at mill scale. Fibre morphology was performed using MorFi fibre analyser (Eymin, Cottin 2003). The rate of macro-fibrils was calculated based on the lengths of fibrils extracted from fibres, relative to the sum of both fibre and fibril lengths. Then, Rapid-Köthen handsheets were produced according to ISO 5269-2 standard. Bulk (ISO 534:1988), breaking length (ISO 1924-2:1994) and tear index (ISO 1974:1990) were measured on these handsheets after conditioning (ISO 186 2002).

RESULTS AND DISCUSSION

Refining of eucalyptus pulp

Focus was paid to a most efficient refining, pulp properties were plotted as a function of energy consumption.

The application of laccase, alone or in combination with a mediator, resulted in a drainage index development with energy consumption similar to the control pulp. However, drainage index had limited correlation with fibre or pulp properties development. Indeed, bulk was affected by enzymatic treatments: for a given energy consumption, treatments led to a bulk reduction (**Figure 2**).

Differences were already observed before some mechanical treatment was applied. Then, increasing refining level reduced differences between modalities. Lower bulk observed for all the biotreated pulps indicated that the fibres were more flexible and more amenable to compaction during the sheet formation. The new mediator alone or laccase + new mediator treatments had the most important effect on the bulk, revealing that the new mediator affected the fibre conformability.

A consequence of these denser handsheets was a stronger pa-

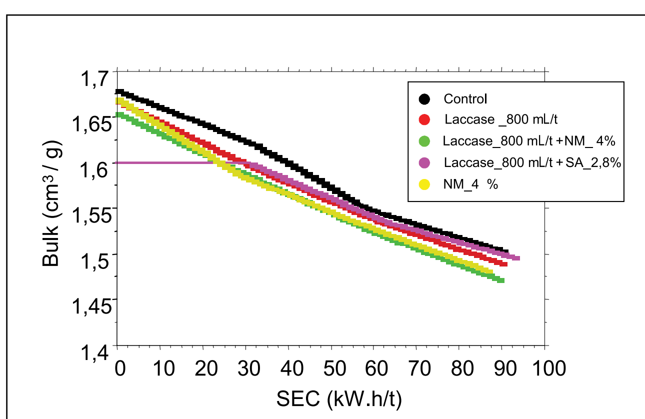

Figure 2. Evolution of bulk of eucalyptus bleached kraft pulp as a function of energy consumption after laccase treatments

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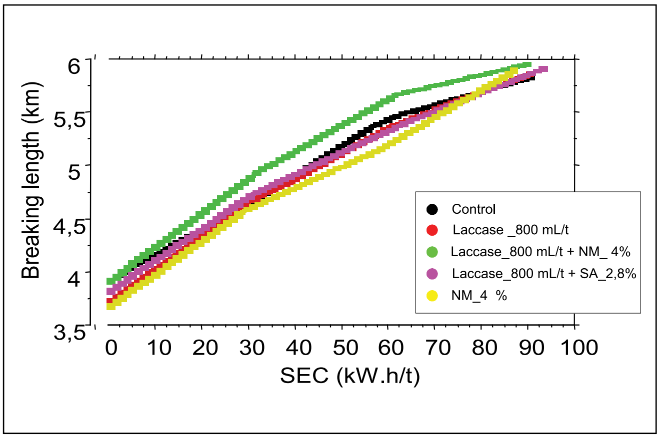

Figure 3. **Evolution of breaking length of eucalyptus bleached kraft pulp as a function of energy consumption after laccase treatments**

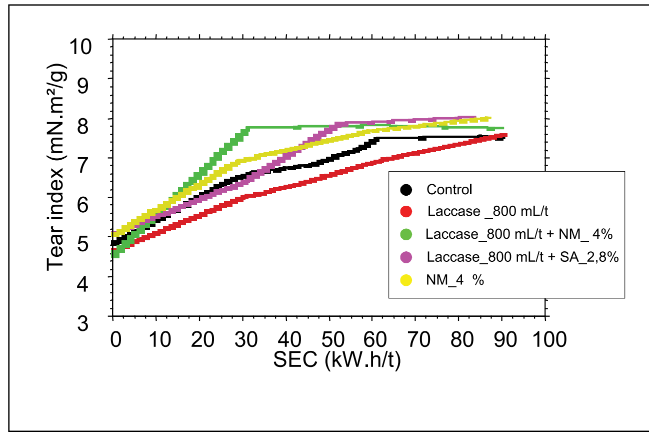

Figure 4. **Evolution of tear index of eucalyptus bleached kraft pulp as a function of energy consumption after laccase treatments**

per, as observed with breaking length (**Figure 3**) and tear index (**Figure 4**) evolutions.

The tensile strength, represented by the breaking length, was improved when the laccase treatment was performed in the presence of the new mediator. Laccase alone, in presence of syringaldehyde or new mediator alone did not modify the development of the tensile strength of this eucalyptus bleached kraft pulp. Besides, some impact on the fibre intrinsic strength was observed, as represented by the evolution of tear index. Laccase + new mediator or the new mediator alone did not affect the fibre intrinsic strength, allowing maintaining the tear index. This was not the case for the other laccase treatments, and especially with the laccase alone, for which a decrease in tear index was observed.

It was therefore interesting to note that the laccase associated to the new mediator allowed to enhance both breaking length and tear index. Generally, the higher the tensile strength and the lower the tear index.

Refining of *Pine radiata* pulp

This type of pulp is used in different paper grades. It is known for its difficulty to be refined, i.e. requiring a lot of electrical energy to reduce bulk and develop bonding properties. Laccase, alone or associated to the new mediator, was used to reach these objectives. The biotreatments facilitated the refining of this pulp: the use of the mediator alone or laccase alone could save electrical energy (**Figure 5).**

There was no synergistic effect between laccase and mediators. Contrary to the observations on eucalyptus pulp, consequences of enzymatic treatments on bulk were none. Moreover, the enzymatic treatment did not modify the development of tensile strength of the pulp during refining.

Based on these observations, laccase treatments had very limited consequences on pulp properties. However, tear index was negatively affected (**Figure 6**). Before refining, lower tear resistances were measured compared to the control. The differences increased with mechanical treatment. Such a trend was explained by a weakening of fibres and a more important fibre cutting phenomenon. This indicated that the fibres were more amenable to the mechanical action and that the fibre fibrillation and cutting needed less energy. This was confirmed by the higher macrofibrillation index observed (**Figure 7**) on the refined

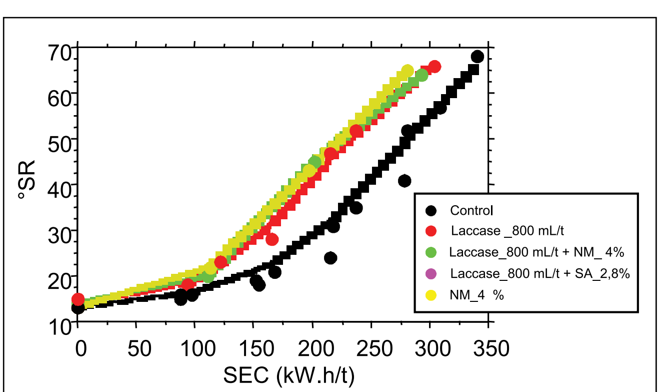

Figure 5. **Evolution of drainage index of *Pine radiata* unbleached kraft pulp as a function of energy consumption after laccase treatments**

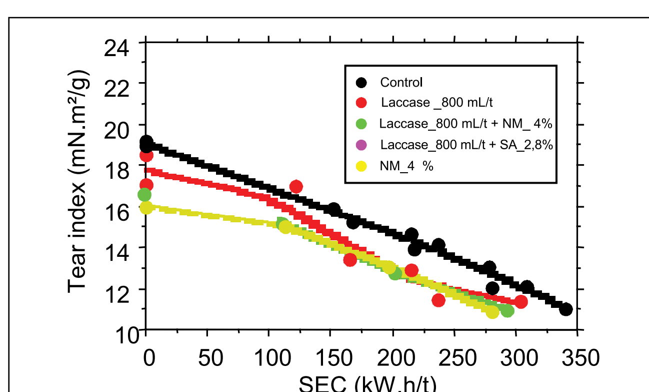

Figure 6. **Evolution of tear index of *Pine radiata* unbleached kraft pulp as a function of energy consumption after different laccase treatments**

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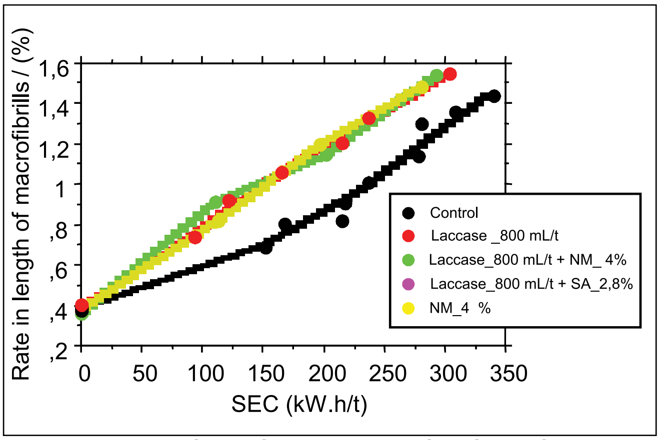

Figure 7. Evolution of macrofibrillation index of the fibres of *Pine radiata* unbleached kraft pulp as a function of energy consumption after laccase treatments

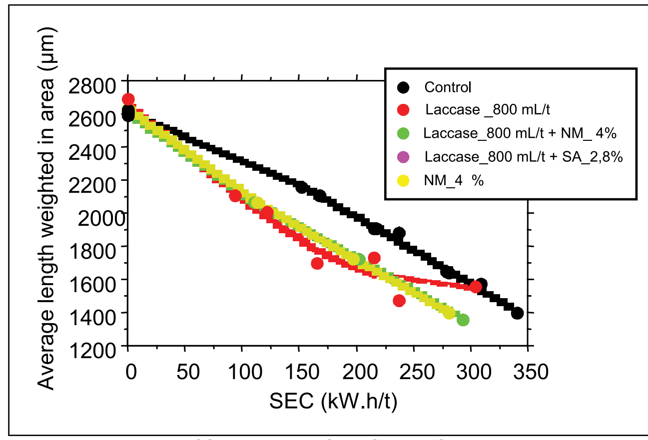

Figure 8. Evolution of fibre length of the fibres of *Pine radiata* unbleached kraft pulp as a function of energy consumption after laccase treatments

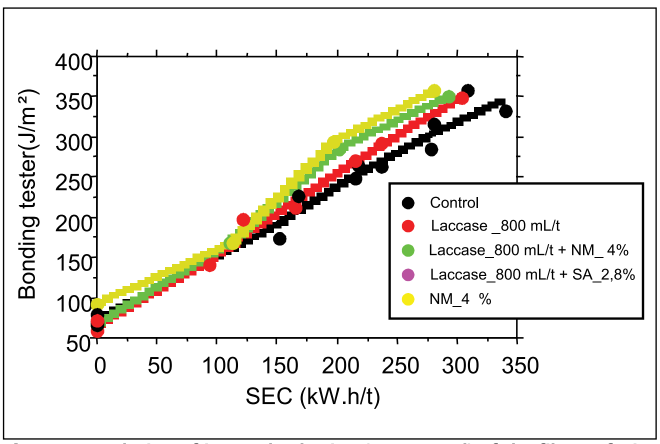

Figure 9. Evolution of internal cohesion (Scott Bond) of the fibres of *Pine radiata* unbleached kraft pulp as a function of energy consumption after laccase treatments

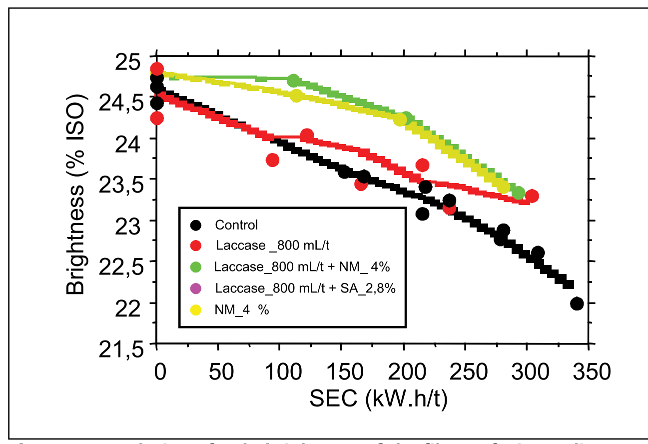

Figure 10. Evolution of pulp brightness of the fibres of *Pine radiata* unbleached kraft pulp as a function of energy consumption after laccase treatments

biotreated pulps and by the reduction in fibre length (**Figure 8**). A consequence of the better fibrillation was measured on internal strength (**Figure 9**).

After the laccase or new mediator treatment, the *Pine radiata* unbleached kraft pulp fibres could develop higher bonding potential at a given energy requirement.

The laccase treatment or the new mediator were interesting alternatives to reduce the refining energy of this *Pine radiata* unbleached kraft pulp. Another interesting result was the impact of such a treatment on the pulp brightness (**Figure 10**).

Some delignification seemed to occur, allowing increasing the pulp brightness. The laccase treatment alone had no significant effect on the pulp brightness because the enzymes can only attack the phenolic compounds, which were already degraded during pulp production. On the contrary, the new mediator and laccase + new mediator were able to oxidise some non-phenolic compounds, which directly affected the pulp brightness.

CONCLUSIONS

The use of laccase on the eucalyptus kraft pulp affected the refining behaviour and the paper sheet formation. A denser and stronger paper could be produced. If a breaking length of 5 km was required by the papermakers, energy savings of 30% and increase in tear index of 10% could be observed.

The use of laccase on the *Pinus radiata* unbleached kraft pulp allowed also some energy savings without degradation of the main physical properties, improving the internal cohesion and the pulp brightness. It could be envisaged the use of laccase alone or the new mediator alone to achieve such results.

Some modification of the refining conditions will be envisaged by varying the refining intensity.

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